Preparation of magnesium aluminate spinel by auto combustion route using glycine as fuel and densification study with Cr_2O_3 addition

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
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In
Ceramic Engineering

By
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2009-2013

CERTIFICATE

This is to certify that the thesis entitled, "Preparation of magnesium aluminate spinel by auto combustion route using glycine as fuel and densification study with Cr_2O_3 addition" submitted by Miss. Swagatika Das (109CR0200) in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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ABSTRACT

The present work deals with the processing and sintering of phase pure Mag–Al spinel by auto-combustion process by using glycine as fuel. Magnesium and aluminium nitrates have been used as the oxidizers and glycine as the fuel. Addition of glycine to the mixture of magnesium and aluminium nitrates results in a series of redox reactions to form a complex which subsequently crystallizes to form spinel at a lower temperature. Mag-Al spinel has been synthesized by varying metal to glycine ratio as 1:2, 1:2.22 and 1:2.5. Variation of Calcination temperature was done from 600°C to 800°C for 2 hours soaking and their XRD analysis were performed to identify the exact starting temperature for obtaining definite phase for pure spinel. The phase pure Mag-Al spinel was formed at 700 °C, for all the composition.Cr_2O_3 is added to the spinel and densification effect was studied. The effect is highest in the Composition 3 that is metal to glycine ratio 1: 2.5. The highest Bulk density was achieved is 3.52 that is for composition 3. Apparent porosity and shrinkage value was also calculated.

INTRODUCTION

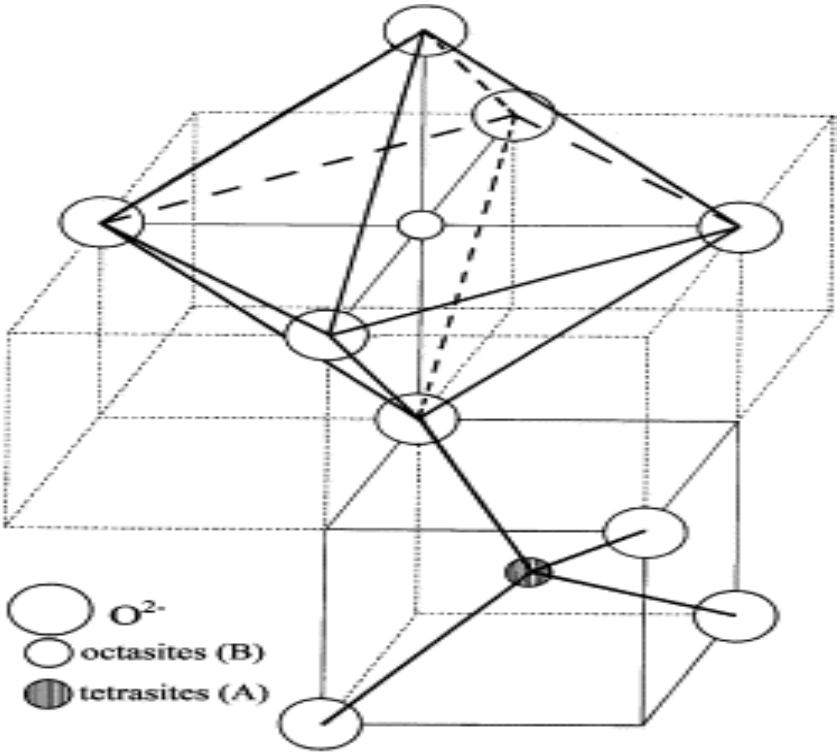
Magnesium alumina spinel ($MgAl_2O_4$) possesses a very rare combination of valuable properties that makes it the first choice material in many structural, chemical, optical and electrical applications. It has very high strength at both elevated and normal temperature, which combined with the fact that it has no phase transition up to the melting temperature (2135°C) recommends it as an excellent refractory material for use. At the same time, it has low thermal expansion coefficient (thus thermal shock resistance), low dielectric constant and high chemical inertness in both acidic and basic environment. Spinel-based materials are used in various applications, such as: humidity sensors, dentistry, nuclear technique, catalyst support, reinforcing fibers, photo luminescent materials, and ceramic pigments.

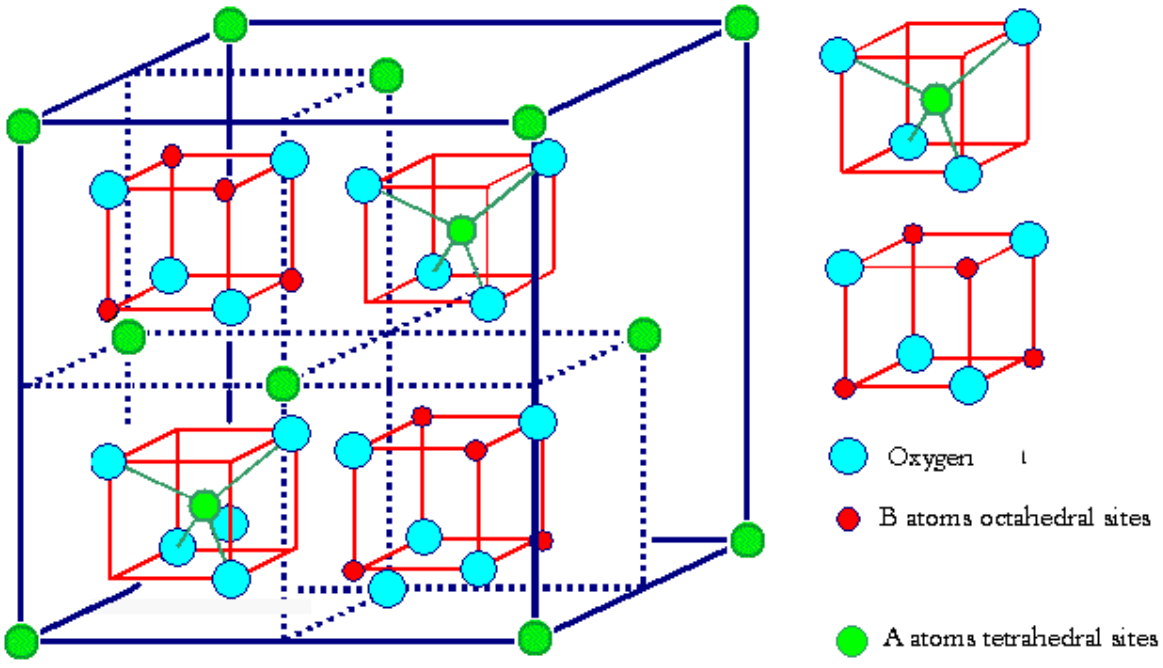
SPINEL:

Naturally occurring spinels can withstand high temperature and is found in metamorophic rocks. It is also present as non metallic inclusions in steel. It has the general compositions AB2O4 where A is divalent ion like Mg, Fe, Mn and Zn and B is trivalent cation like Al^{+3},Fe^{+2} .

SPINEL STRUCTURE:

Spinel group of minerals have the general formula AB_2O_4 where A is divalent (+2) cation and B is (+3) cation. The space group of spinel is Fd3m (227) with number of tetrahedral 'a' and octahedral d sites filled are 8 and 16 respectively [1]. Divalent sites are located on 'a' tetrahedral sites and the tetravalent cations are located on octahedral sites. Generally, Spinels are denoted by formula AB_2O_4 and inverse spinels are denoted by $B(AB)O_4$. The intermediate cation distribution has formula $(A_{1-x}B_x)$ $[B_{2-x}A_x]O_4$, where x is a inversion parameters having value range lies between $0 \leq x \leq 1$[2,3,4].



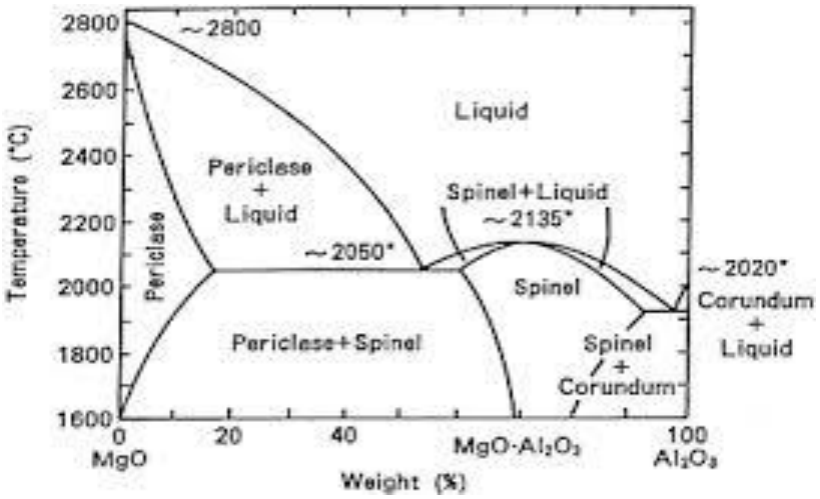


Normal Spinel structure

NORMAL AND INVERSE SPINELS:

In spinel the octahedral can be filled with B (trivalent) atoms and the tetrahedral with (divalent) atoms. The no of octahedral voids are twice than tetrahedral and spinel has AB_2O_4 as formula.. In the "normal spinel" structure, all the divalent cations are located on tetrahedral void sites, while all trivalent cations are on octahedral sites [5]. Generally, Spinels are denoted by formula AB_2O_4 and inverse spinels are denoted by $B(AB)O_4$. The example of normal spinel is chromite and magnetite is an inverse spinel [6].

PHASE DIAGRAM OF MgO-Al_2O_3



The binary phase of MgO and Al_2O_3 are shown in diagram above. From the diagram it is clear that the melting point of magnesia is 2800^{o}C and alumina is 2020^{o}C. At 50:50 molar compositions of MgO and Al_2O_3 the spinel phase formation occurs. The spinel formed is a eutectic compound which has a congruently melting nature. Melting point of spinel is around 2135°C. The spinel divides the whole system into two independent eutectic systems which are given by MgO-$MgAl_2O_4$ and $MgAl_2O_4$-Al_2O_3 as shown in the diagram. So if a stoichiometric composition of MgO and Al_2O_3 is taken, heated and cooled down slowly then at eutectic point, it gets converted to pure spinel. The $MgO.Al_2O_3$ system is interesting to the refractory technologists, because spinel $MgO.Al_2O_3$ itself is a refractory and no liquid formation takes place at any temperatures below 1900°C. The reaction between equimolecular amounts of magnesia and alumina results in a substantial volume expansion. This composition or one higher in magnesia composition can be made to produce steel-tight basic lining products.

IMPORTANCE OF MAGNESIUM ALUMINATE SPINEL:

Mag-Al spinel is used for refractory as well as structural applications at elevated temperatures due to its high melting point, excellent mechanical strength and impressive chemical resistance. It is the most Stable compound present in the $MgO\text{-}Al_2O_3$ system. It is chemically compatible with alumina, zirconia and mullite, hence spinel is good phase for ceramic matrix composite [7]. The major application areas of spinel refractory are burning zones of cement rotary kilns [8], sidewalls and bottom of steel teeming ladles and checker work of glass tank furnace generators because of its resistant to corrosion by slag. Alumina rich or magnesia rich matrix is suitable for spinel, depending upon the temperature and environment zone where it is used. Thus Mg rich and Al rich are very much used in refractory applications. Compounds which are having this type of Spinel structures are used for electrochemical uses, electrical applications and also used in semiconductor devices for semi conduction like in solar cell and in the biological applications.

Magnesia alumina Spinel can be used extensively as a replacement for chrome ore in basic brick manufacture. It imparts the improved thermal shock resistance which is normally associated with chrome additions, but without the potential problem of hazardous waste disposal of it. This improved thermal shock resistance is achieved due to the development of internal micro cracks and voids due to the mismatched thermal expansion rates. The reversible thermal expansion of this Spinel is approximately half that of the magnesia. The most used area of magnesia spinel bricks is in cement rotary kilns where they have demonstrated superior properties compared to that of previously used mag-chrome bricks. This extended life has been attributed to the ability of the spinel bricks to retain a coating without excessive penetration and peeling. This Spinel can be used as a replacement for chrome in some other applications where the disposal of used chrome containing refractories is a major problem, such as lime kilns and glass tank regenerator checkers. Spinel has a small amount of free magnesia which can be used to design aluminous refractories. The free magnesia will react with available alumina to form secondary spinel. The volume expansion due to the reaction of one mole of magnesia with one mole of alumina, to form spinel, measured by technical sintering, is 5 percent. Thus, the addition of spinel to aluminous bodies will impart some volume expansion. The free magnesia in the spinel can also be used as a setting agent for phosphate bonds to produce a cold setting monolithic refractory or mortar [9].

Magnesium aluminate spinel is an advanced ceramic material having useful mechanical properties even at extreme temperatures hence is an important material for high temperature application. Mag-Al spinel is a highly refractory material because of its high melting point. Superior strength at ambient and elevated temperatures, better corrosion, erosion, abrasion resistance and thermal spalling resistance are few of its remarkable properties which makes it an excellent refractory material.

Due to above stated reasons it is used for application in side-walls and the bottom of steel teeming ladles, burning and transition zones of cement rotary kilns etc [10, 11]. It is used as a major component in an alumina rich or magnesia rich matrix, according to its environmental condition of the application zones. Hence Magnesia or alumina rich spinel composition is important for application point of view. Being an important refractory material it can also be used in advanced application like high-temp arc-enclosing envelops, humidity and infrared sensors, transparent windows, domes and armour material [12].

Additives are foreign substances which are intentionally added to provide promotion effects in processing and which ultimately improves the final properties. An additive forms a solid solution, or a new compound or a liquid phase either of its own composition or of a new composition by reacting with the batch materials. In a solid solution, both interstitial and substitutional effects may occur, causing a vacancy and or strain in the lattice and this ultimately promotes diffusion dependent processes.

The introduction of a lower valence cation creates anion vacancy (or cation interstitial), which increases the diffusivity and all diffusion dependent processes, as is the case of Li_2O doping for sintering of MgO [13]. Incorporation of a higher valence cation creates cation vacancies rather than forming anionic interstitial [14] and thus increases the cation diffusion rate and related processes. The formation of a liquid phase acts as a lubricant, produces higher diffusivity than solid phase, attracts the wetted solid particles by capillary force of attraction and results in better compaction. For magnesium aluminate spinel system additives can affect synthesis and formation, sintering, growth, properties, etc. Additives are most important for the formation and sintering of magnesium aluminate spinel.

Additives for spinel can be broadly classified as two types: additives for spinel formation and additives for sintering.

This present work deals with the processing and sintering of phase pure Mag-Al spinel synthesized by auto-combustion process. Magnesium and aluminium nitrates have been used as the oxidizers and glycine as the fuel. Addition of glycine to the mixture of

magnesium and aluminium nitrates results in a series of redox reactions to form a glycine - nitrate complex which subsequently crystallizes into spinel at a lower temperature. Results on the phase evolution and powder sinterability have been reported with the addition of Cr_2O_3. A probable mechanism for low-temperature densification has also been suggested.

LITERATURE REVIEW

PREPARATION METHODS FOR SPINELS:

The fabrication methods of spinel refractory and the $MgO\text{-}Al_2O_3$ phase diagram have been known since the last two decades [15]. But spinel was not much successful till 1980's because of complexity in the process parameters. Spinel formation from Alumina and Magnesia is associated with high (5-7%) volume change, hindering the densification process [16].

Thus a two-stage firing process was applied. The first step starts with getting the precursors being calcined at an intermediate temperature, and the second step continued with sintering/densification of the formed spinel around $1600^oC\text{-}1800^oC$. The preparation method of dense spinel products has improved over the years. The preparation of spinel by different routes has been reported in different years [17].

Conventional sintering technique takes place at higher temperatures and requires longer reaction time such that the synthesized powder from agglomerate and of low sintering activity. Various methods used are sol gel, co precipitation [18], spray drying and normal micelle method. There are many advantages in these methods such as high purity and sinterability of the produced powders. Ultrafine homogeneous powders of single phase spinel are useful for low temperature densification. Combustion synthesis process [19] is suitable for synthesizing powders for advanced applications. Ultrafine oxide ceramic powders of Al_2O_3, ZrO_2, $BaTiO_3$, $LaCrO_3$, and Y_2O_3–ZrO_2 are manufactured by combustion synthesis using the exothermic redox reaction between an oxidizer and a fuel. The fuels used are source of C and H and liberate heat which help in the formation of metal ion complexes facilitating mixing of the cations in solution. The advantages of combustion synthesis being:

- ✓ Comparatively simple equipment is used
- ✓ High purity products are formed.
- ✓ Metastable phases are stabilized
- ✓ Virtually any size and shape product are formed.

Both the stoichiometric and non-stoichiometric Mag-Al spinel has been prepared by combustion synthesis route using urea as fuel source and metal nitrates as the oxidizers. Citric acid addition to the mixture of $Mg(NO_3)_2$ and $Al(NO_3)_3$ involves a series of redox reactions forming a citrate –nitrate complex crystallizing to form spinel at a relatively lower temperatures. Spinel crystallization by

mixed oxide route from $MgO\text{-}Al_2O_3$ powders is not easy because of lower free energy of calcined oxides. The powders synthesized by most of the chemical methods are amorphous in nature thus are easy to crystallize. Calcination at elevated temperatures did not change the peak position rather sharpened the peaks in terms of intensity, indicating higher crystallite size [20].

Two events that occur during combustion are

- Heat generation during combustion
- Evolution of gas

Heat of combustion results in the crystallization and the formation of the desired phases. High flame temperature affects powder characteristics such as increase in crystal size, hard agglomerates formation and thus decreasing the surface area and sinterability. Powder characteristics are monitored by heat of combustion and gas evolution which are dependent on the fuel nature and ratio of oxidant to fuel.

If fuel is deficient an impure product is obtained as the exothemicity and the associated flame temperature are not sufficiently high enough.

As the flame temperature goes higher, the crystal size increases and the surface area decreases [21].

Thermodynamics of the combustion reaction shows variation in the amount of gases produced and flame temperature with fuel to oxidiser ratio.

I. At 40% fuel- there is No flame, small amount of sparking, and light black product is produced.
II. At 80% fuel- there is little flame, and blackish product is formed
III. At 120% fuel- there is little flame, and dark black product is formed.

Black product denotes the incomplete combustion process [22].

Various additive effects on the magnesium aluminate was studied by different researchers for a long time. Noda and Hasegawa studied the effects of salt vapour on the synthesis of magnesium aluminate.

The influence of the addition of salt vapours was complex. They indicated increased crystal growth especially of alkali fluorides. The effectiveness of the salts follows the following order: LiX>NaX>KX, MgX_2>CaX_2>SrX_2>BaX_2, AF>ACl and BF_2>BCl_2, where A is alkali metal, B is alkaline earth metal and X is fluorine or chlorine.

Helmut [23] studied different additives effect on spinel formation and reported a decreasing order of beneficial effects for the additives V_2O_5, B_2O_3, MoO_3, P_2O_5, WO_3, LiF and MgF_2. MgO, MnO, CaO and NiO are reported to have little effect, and CoO, Li_2O, SiO_2 and Cr_2O_3 are reported to inhibit the reaction. Bhattacharya and others [24, 25] studied the mineralization effect of B_2O_3 up to 1.5 mass % on spinel formation. Higher amounts of additive are observed to form $Mg_3B_2O_6$ on cooling and mineralization was affected. Initially an Mg-borate liquid phase was formed, which at higher temperatures dissolves alumina, thus leading to the formation of a magnesia-modified boro-aluminate glass.

Ju and co-workers reported improved thermal shock resistance for periclase spinel refractories by addition of a small amount of Cr_2O_3 as chrome concentrate. Cr_2O_3 was found to form a spinel solid solution thus exhibiting increased melting loss resistance with increased Cr_2O_3/Al_2O_3 and Cr_2O_3/Fe_2O_3 ratios. The effect of the addition of Cr_2O_3 up to 4 mass% was studied by Sarkar et al. on spinel compositions with MgO: Al2O3 molar ratios of 2:1, 1:1 and 1:2. They found that Cr_2O_3 showed the greatest effect on densification for alumina rich spinel. Cr_2O_3 was reported to reduce the temperature of complete solid solubility of excess alumina in spinel for the alumina rich composition but no Cr-bearing phase was found. It was reported that the cold and hot strengths deteriorated for all the compositions and the deleterious effect was more for the batches containing higher amounts of additive. Cr_2O_3 was also observed to be effective for grain growth, especially for the alumina rich compositions.

OBJECTIVES OF THE WORK

- ✓ To synthesize phase pure Mag-Al spinel at low temperature.
- ✓ Use of glycine as fuel in the auto combustion synthesis of magnesium aluminate spinel.
- ✓ Observe the change in Mag-Al spinel phase formation temperature with variation in metal: glycine ratio and calcination temperature.
- ✓ Densification study of Mag-Al spinel synthesized via auto combustion synthesis route using glycine as fuel and Cr_2O_3 as additive.

EXPERIMENTAL WORK

SYNTHESIS OF Mag-Al SPINEL

RAW MATERIALS USED ARE:

- Magnesium nitrate hex-hydrate AR (MERCK LTD.)
- Aluminium nitrate Nona-hydrate GR (LOBA CHEMIE PVT. LTD)
- Glycine acid (FISCHER SCIENTIFIC)
- 3% Poly vinyl alcohol

STOCK SOLUTION PREPARATION:

0.5 M both $Al(NO_3)_3.9H_2O$ and $Mg(NO_3)_2.6H_2O$ solution was prepared.

A. For 0.5 M $Mg(NO_3)_2.6H_2O$ solution, 128.2 g of salt was taken in a 500 ml beaker.

B. For 0.5 M $Al(NO_3)_3.9H_2O$ solution, 187.56 g of salt was taken in a 500 ml beaker.

1 lit. $Mg(NO_3)_2.6H_2O$ solution & 2 lit. $Al(NO_3)_3.9H_2O$ solution was prepared.

OXIDISER TO FUEL RATIO CALCULATION:

Oxidation / reduction valency of

- ✓ $Mg(NO_3)_2.6H_2O = +2+2(0+(-6))$

  $= +2-12$

  $= -10$

- ✓ $Al(NO_3)_3.9H_2O = +3+3(0+(-6))$

  $= +3-18$

  $=-15$

- ✓ GLYCINE = $C_2H_5NO_2 = 2*(+4)+5+0-4$

  $= 8+5-4$

Reducing spices	
ELEMENT	VALENCY
Al^{+3}	+3
C	+4
H	+1

Oxidising spices	
ELEMENT	VALENCY
O^{-2}	-2
N	0

= +9

In spinel Mg : Al = 1:2

Total valency of oxidiser = (-15)+(-5)

=-20

Fuel valency = +9

Stoichiometric oxidiser to fuel ratio is = 20/9 = 2.22

So, **the stoichiometric combustion ratio where complete combustion takes place = 1:2.22**

That is why we decided to take three compositions that is fuel lean, stoichiomertic and fuel rich.

- Three compositions are :-

I. Composition 1: - N:G = 1:2

II. Composition 2: - N:G = 1:2.22

III. Composition 3: - N:G = 1:2.5

Calculation of glycine amount:

Composition 1:

50 ml of $Mg(NO_3)_2.6H_2O$ solution and 100 ml of $Al(NO_3)_3.9H_2O$ solution was taken.

So, total nitrate solution was 150 ml. and 0.5 M solution.

For 1:2 composition 150 ml. ,1 M glycine solution was required.

150 ml, 1M glycine solution = (75 /1000)*150 = 11.25 g

So, for composition 1 (where oxidiser to fuel ratio is 1:2)

We took 50ml of $Mg(NO_3)_2.6H_2O$ solution

100 ml of $Al(NO_3)_3.9H_2O$ solution

& 11.25 g of glycine

Composition 2:

50 ml of Mg $(NO_3)_2.6H_2O$ solution and 100 ml of Al $(NO_3)_3.9H_2O$ solution was taken.

So, total nitrate solution was 150 ml. and 0.5 M solution.

For 1:2.22 composition 150 ml. ,1.11 M glycine solution was required.

150 ml, 1M glycine solution = (75 /1000)*150 = 11.25 g

150 ml, 1.11 M glycine solution = 11.25 * 1.11 = 12.48 g

So, for composition 2 (where oxidiser to fuel ratio is 1:2.22)

We took 50ml of Mg $(NO_3)_2.6H_2O$ solution

100 ml of $Al(NO_3)_3.9H_2O$ solution

& 12.48g of glycine

Composition 3:

50 ml of Mg $(NO_3)_2.6H_2O$ solution and 100 ml of Al $(NO_3)_3.9H_2O$ solution was taken.

So, total nitrate solution was 150 ml. and 0.5 M solution.

For 1:2.5 composition 150 ml. ,1.25 M glycine solution was required.

150 ml, 1M glycine solution = (75 /1000)*150 = 11.25 g

150 ml, 1.25 M glycine solution = 11.25 * 1.25 = 14.06 g

So, for composition 2 (where oxidiser to fuel ratio is 1:2.22)

We have to take 50ml of Mg $(NO_3)_2.6H_2O$ solution

100 ml of $Al(NO_3)_3.9H_2O$ solution

& 14.06g of glycine

COMBUSTION SYNTHESIS:

Composition 1:

- ✓ 150 ml. of stock solution was taken in a 250 ml. beaker and 11.25 gm. of glycine as a fuel was added, a magnetic needle (for stirring) was put into the beaker.
- ✓ The beaker was placed on a hot plate (spinot) & both stirring and heating were done simultaneously.
- ✓ After continued heating for 2-3 hours, the solution converted to gel like liquid and finally combustion took place leaving behind a black mass.
- ✓ After cooling, the black mass was collected in a plastic pouch and named COMP 1.

Composition 2 & 3 :- As done for composition 1.Only glycine amount would be 12.48 g & 14.06 g respectively.

GENERAL CHARACTERIZATION:

DIFFERENTIAL SCANNING CALORIMERTRY AND THERMOGRAVIMETRY TEST

The samples having different metal to glycine ratio were characterized by DSC-TG (NETZS, GERMANY) at constant heating rate of 10°C/min in the temperature range of 30°C to 600°C. Data was collected and graphs were plotted.

CALCINATION AT VARIOUS TEMPERATURES

Small amount of all the samples (COMP1,COMP 2 & COMP 3) were taken in different clean and dry alumina crucibles & put in furnace and calcined at various temperatures (600°C,700°C & 800°C) for 2 hours soaking period at heating rate of (3-5)°C/minute.

NOMENCLATURE OF THE SAMPLES

Composition 1(MA 1)- N:G = 1:2

Calcination temperature 600°C – MA11

700°C – MA12

800°C – MA13

Composition 2(MA 2)- N:G = 1:2.22

Calcination temperature 600°C – MA21

700°C – MA22

800°C – MA23

Composition 3(MA 3)- N:G = 1:2.5

Calcination temperature 600°C – MA31

700°C – MA32

800°C – MA33

XRD ANALYSIS OF CALCINED POWDERS

After Calcination X-Ray Diffraction was performed using Philips X-Ray diffractometer PW 1730 with nickel filtered Cu K_α radiation (λ=1.5406A0) at 40 kV and 30mA. The scanning rate was set to 3°C per min and scanned continuously in the range of 15° to 65°C .

ADDITION OF Cr_2O_3:

2 wt % of Cr2O3 was mixed with the magnesia alumina spinel in three different compositions by wet mixing using acetone. After that that is put inside a dryer. Three different compositions were made.

PELLETIZATION

The three different compositions (with the addition of **Cr_2O_3, 2 wt%)** were selected for circular pellet preparation. The selected calcined powders were mixed with 3 vol% PVA, an organic

binder and ground with the help of a mortar and pestle. The three different powders were weighed differently and uniaxially pressed (CARVER, USA) at 2 tons with 30 sec. dwelling time.

SINTERING

The sintering was carried out in a chamber furnace at different temperatures like 1500°C, 1550°C, 1600°C.The heating rate in the furnace was 5°C /minute. The samples were held for 2 hours at these temperatures.

XRD ANALYSIS OF FIRED SAMPLES:

After sintering at 1500°C X-Ray Diffraction was performed using Philips X-Ray diffractometer PW 1730 with nickel filtered Cu K_α radiation (λ=1.5406A0) at 40 kV and 30mA. The scanning rate was set to 2°C per min and scanned continuously in the range of 18° to 48°C.

SHRINKAGE CALCULATION:

The original sample diameter before sintering was measured as 15 mm. After sintering the pellet diameter was measured and shrinkage was calculated according to the formula

SHRINKAGE = (DIAMETER BEFORE SINTERING – DIAMETER AFTER SINTERING)*100/ DIAMETER BEFORE SINTERING

APPARENT POROSITY AND BULK DENSITY CALCULATION:

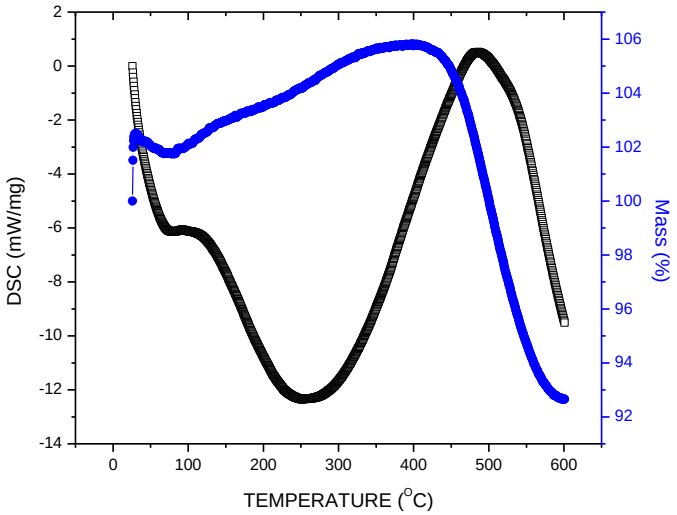
The bulk density and apparent porosity of the sintered pellets were calculated by Archimedes principle using kerosene. Dry Weight is measured and then the pellets were kept in karosene and then vacuuming is done for about 2 hrs. After that suspended weight is measured using apparatus in which pellet is suspended in kerosene. After the suspended weight, soaked weight is taken. Hence the dry weight, soaked weight and suspended weight were measured accurately. The bulk density and apparent porosity were calculated by using the formulas:

Bulk density= Dry weight/(Soaked wt-Suspended wt)

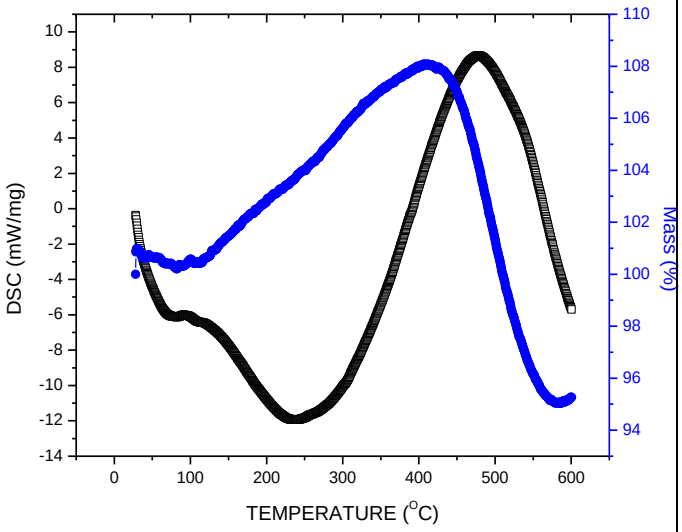
Apparent porosity= (Soaked wt- Dry wt)/ (Soaked wt – Suspended wt) x 100

RESULT & DISCUSSION

DSC/TG for three different compositions

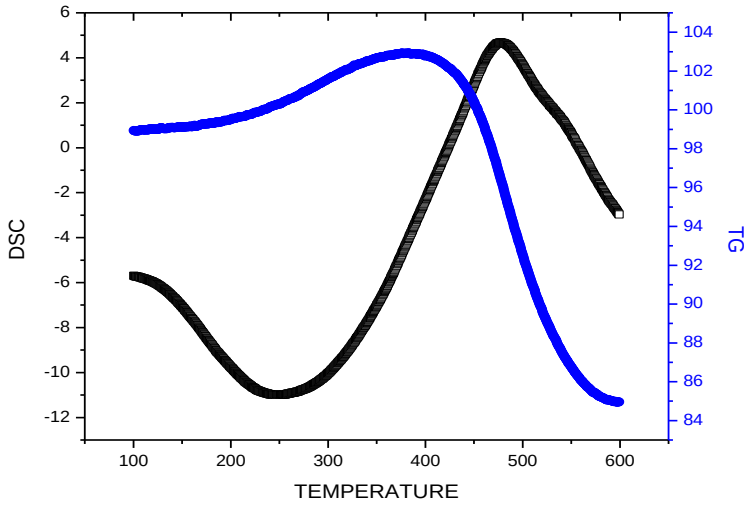


COMPOSITION 1



COMPOSITION 2

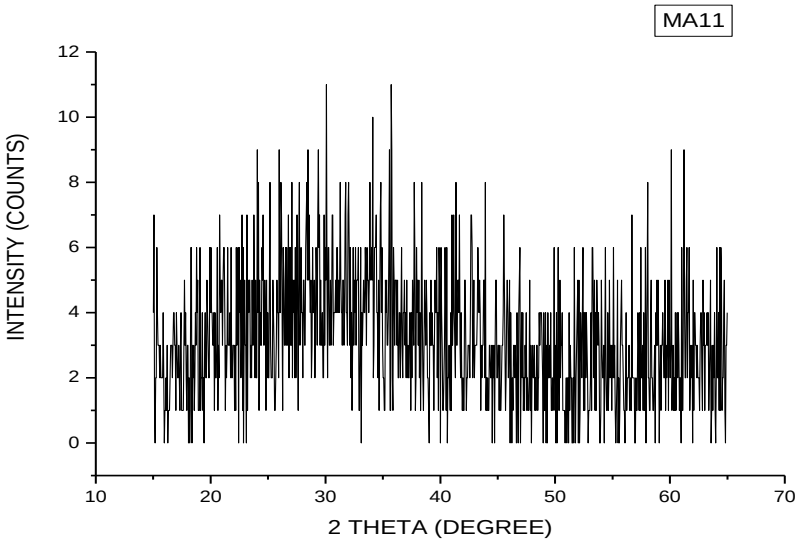
COMPOSITION 3



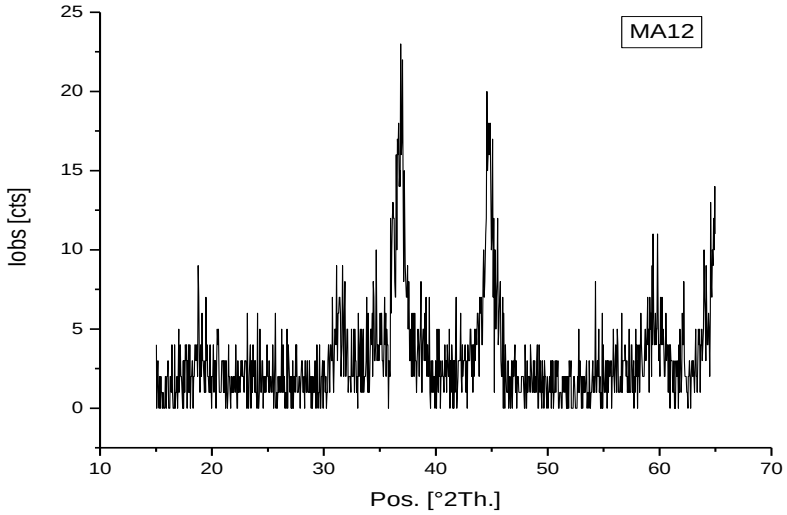
There is gradual loss of weight up to 600 ˚C which indicates that there is huge amount of organic volatile materials present in the samples or in glycine. The weight loss may also be due to decomposition of nitrates present in the samples. In the composition 3, the reaction starts at a lower temperature compared to others.

XRD for COMP 1 in three different temperatures that are 600˚C,700˚C & 800˚C

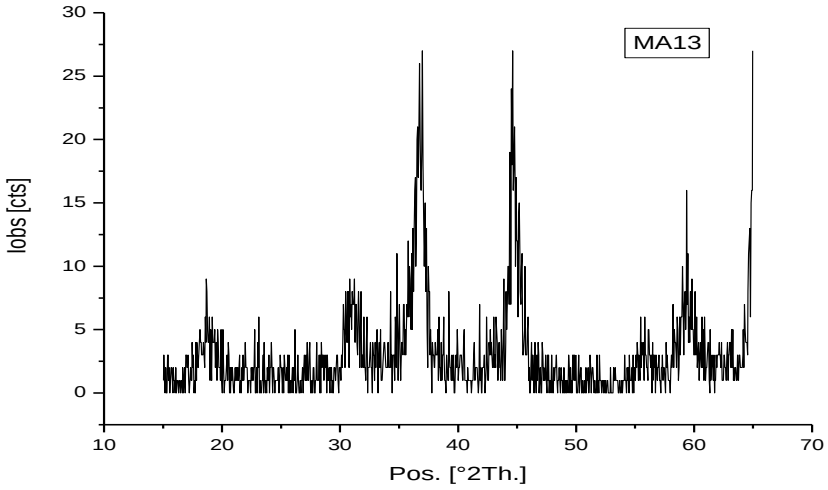
600˚C



700˚C

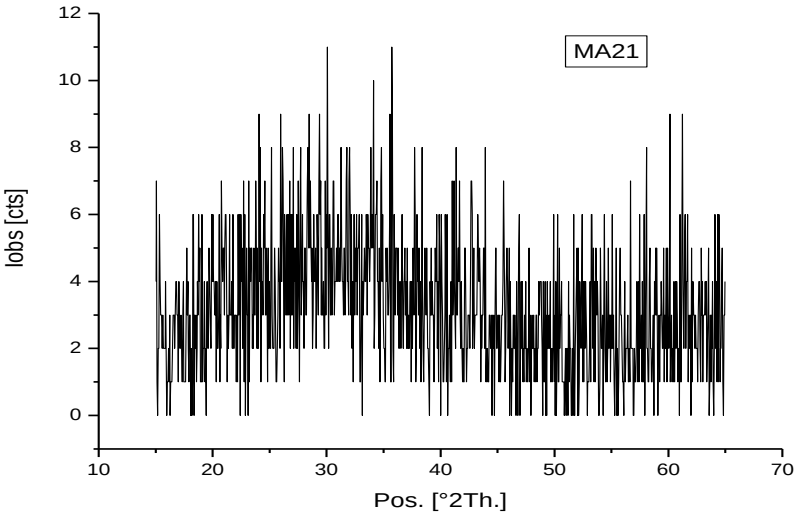


800˚C

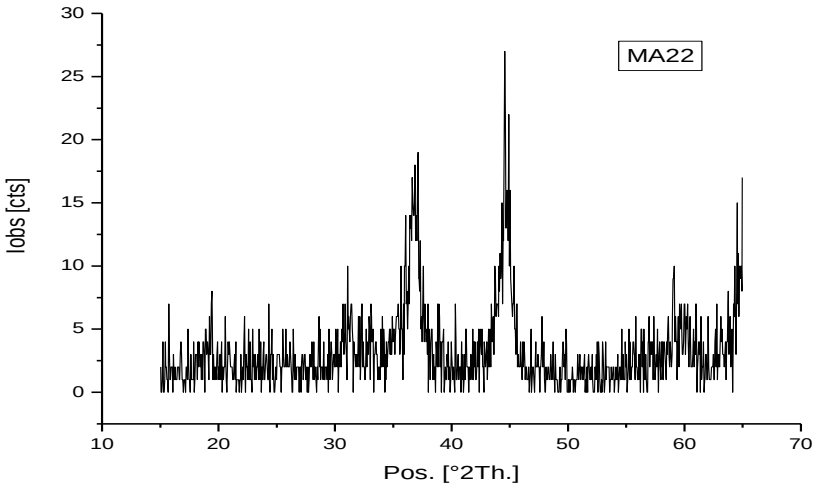


XRD for COMP 2 in three different temperatures that are 600˚C,700˚C & 800˚C

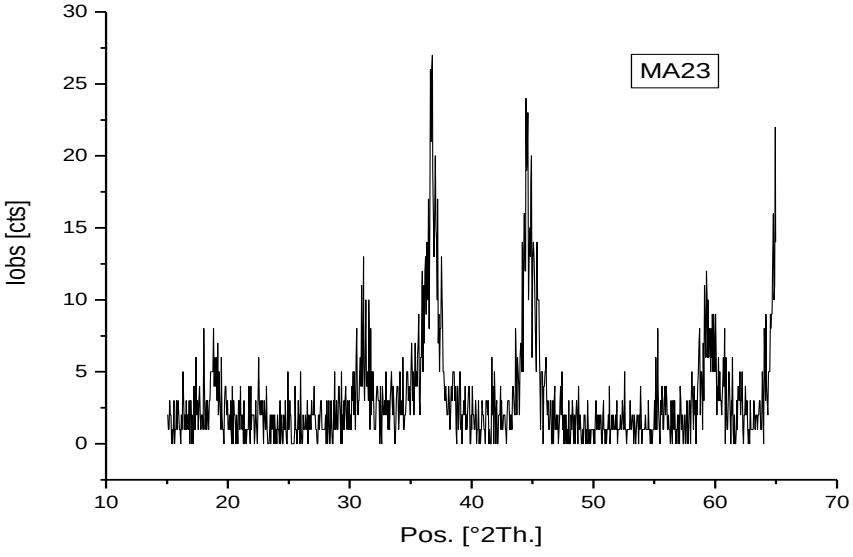
600˚C



700˚C

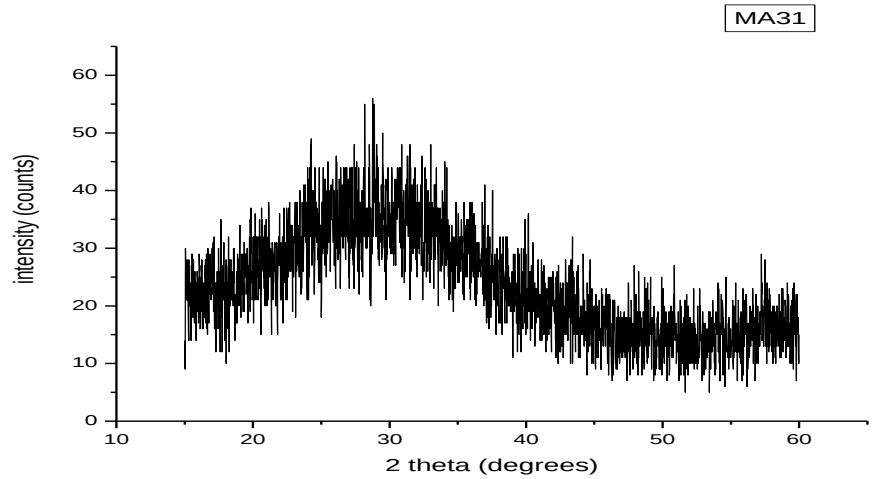


800˚C

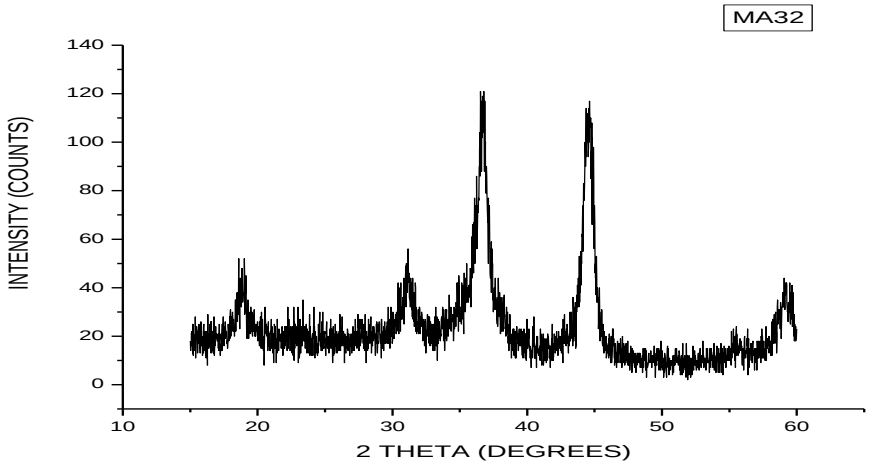


XRD for COMP 3 in three different temperatures that are 600˚C,700˚C & 800˚C

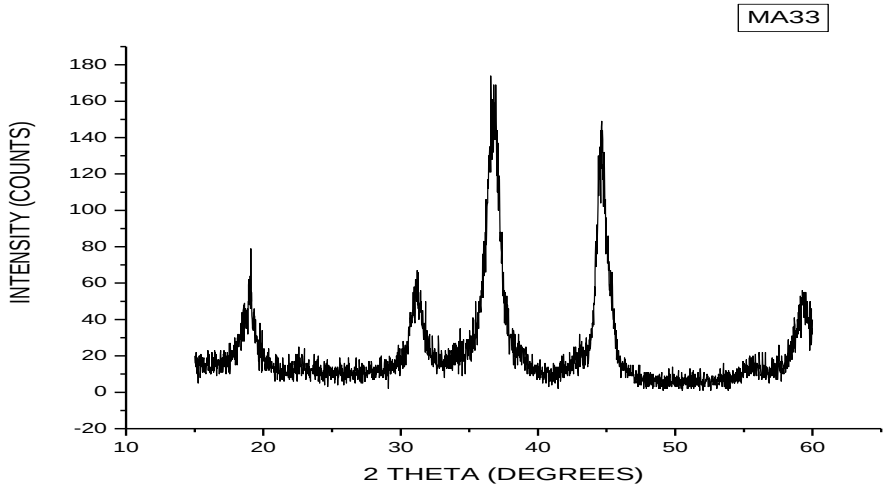
600˚C



700˚C



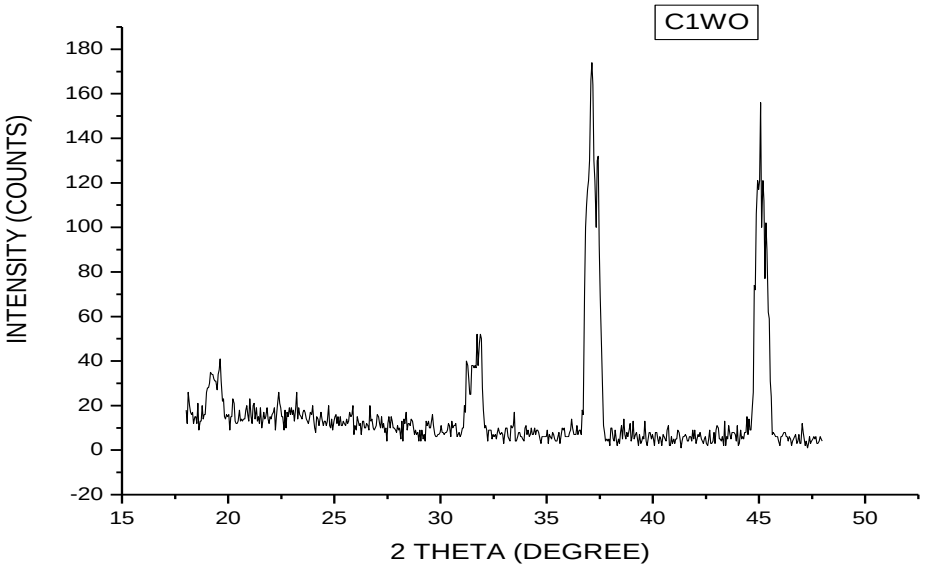
800˚C



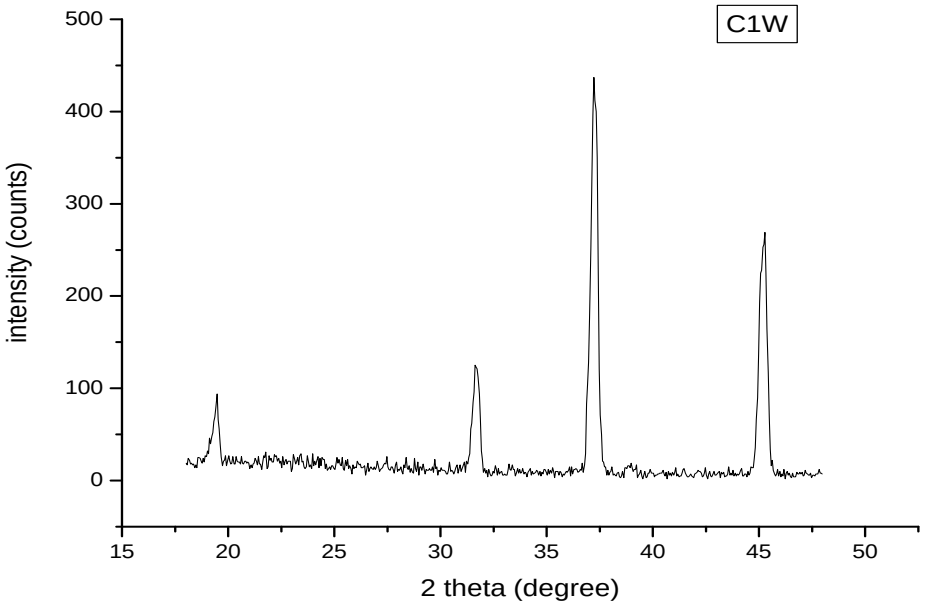
In all the three compositions 600 C calcination shows diffused, and very poorly crystalline material and does not show the formation of spinel phase. Increase in calcination temperature to 700 C and above confirms the spinel phase for all the compositions and 700 C calcined products were selected for sintering study. Developed spinel phase in C3 composition was found to have stronger peaks, indicating higher extent of spinel formation in the batch.

Composition 1

Without Cr_2O_3

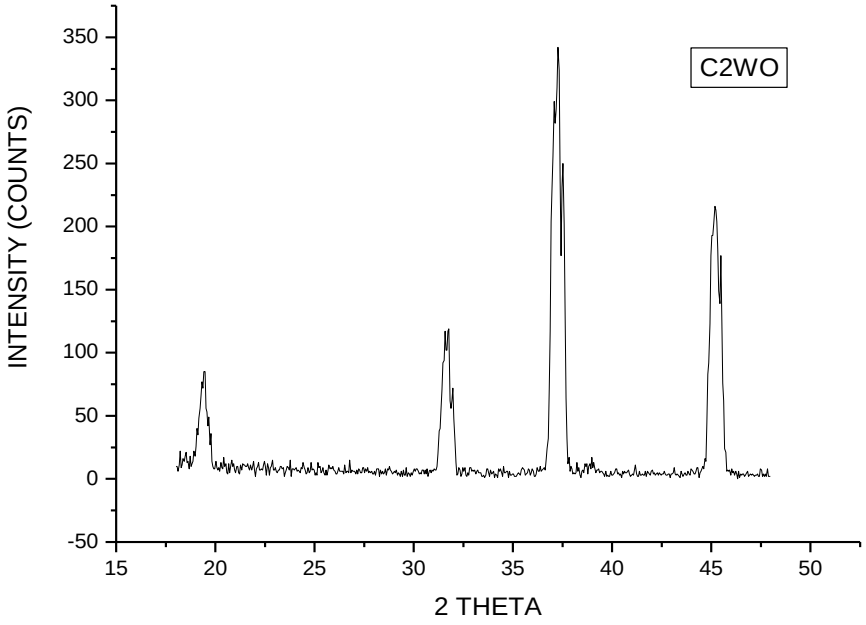


With Cr_2O_3

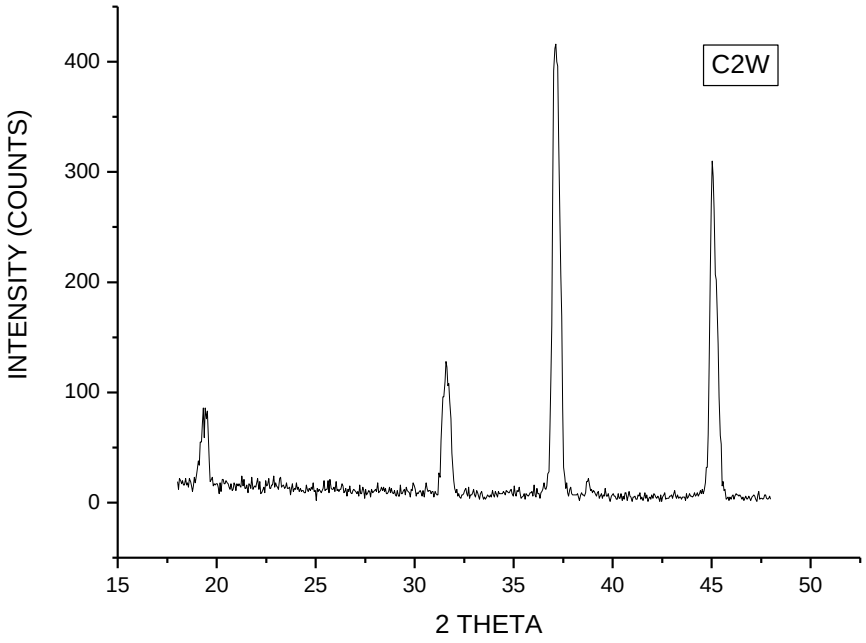


Composition 2

Without Cr_2O_3

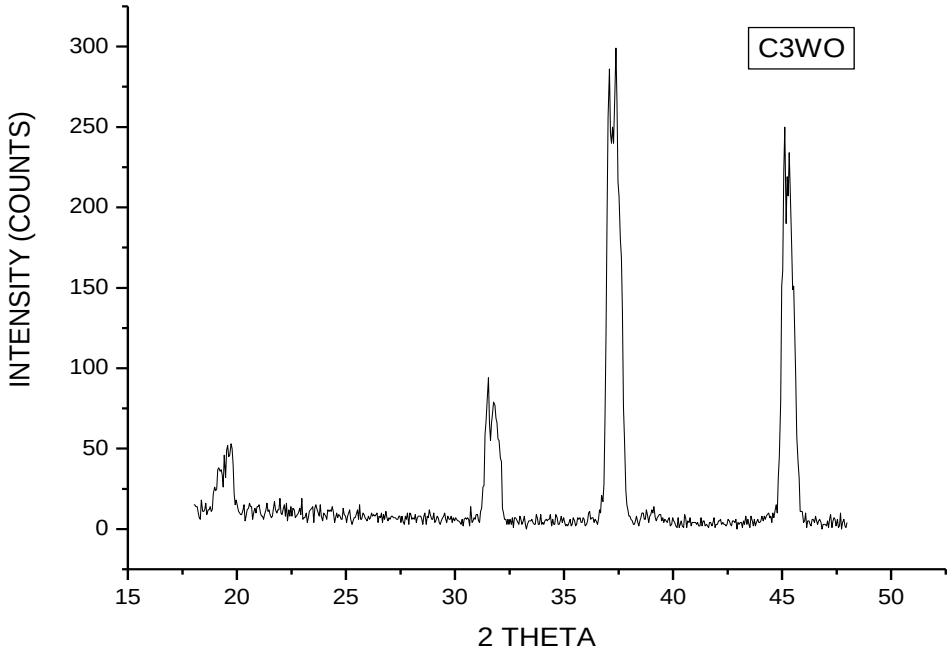


With Cr_2O_3

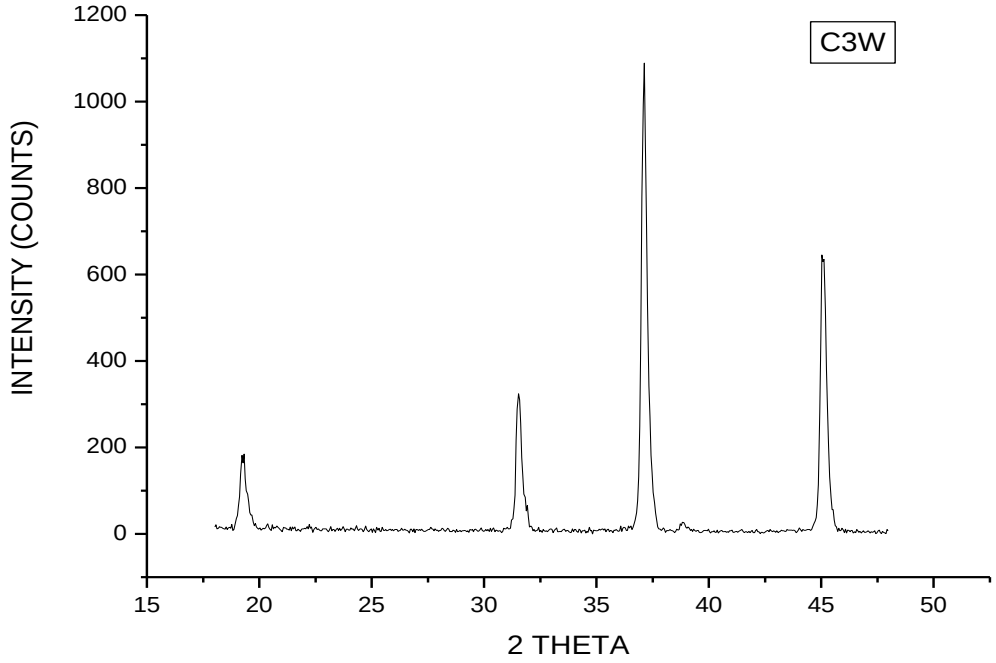


Composition 3

Without Cr_2O_3



With Cr_2O_3

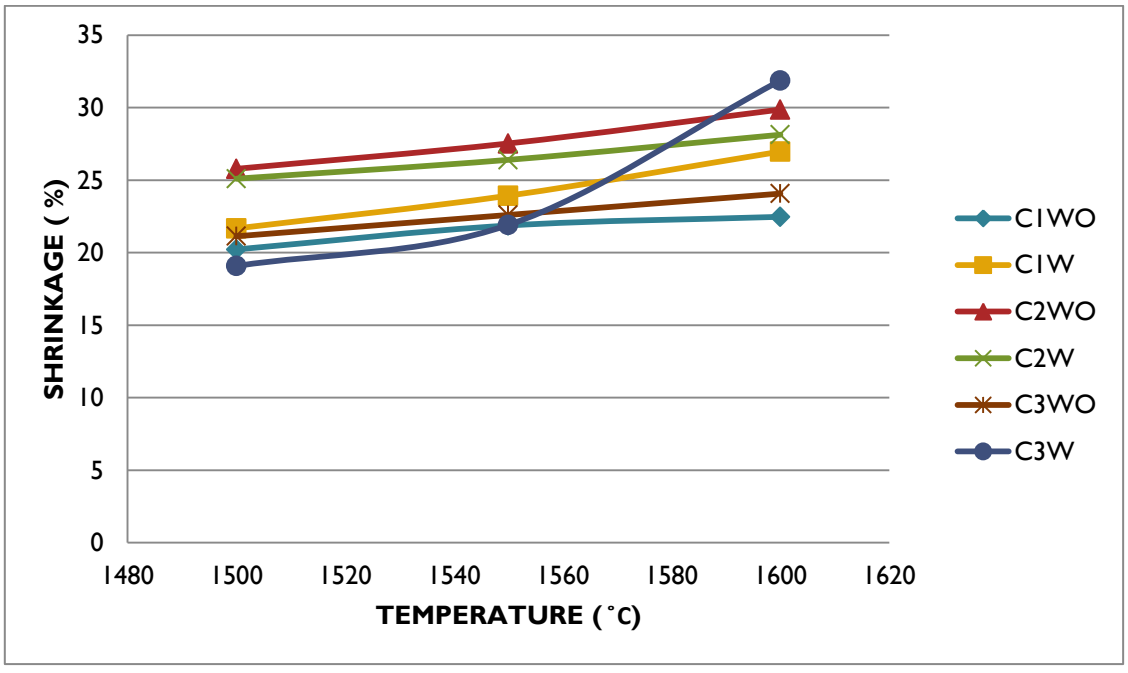


For all the three compositions 1500 C sintered products were characterized for phase analysis. Addition of Cr2O3 was found to enhance the spinel content of all the compositions. The effect was found to be pronounced for the composition C3.

Calculation of Shrinkage

COMP/TEMP(˚C)	C1WO	C1W	C2WO	C2W	C3WO	C3W
1500	20.22	21.67	25.78	25.1	21.13	19.08
1550	21.87	23.93	27.53	26.4	22.6	21.91
1600	22.47	26.97	29.87	28.13	24.07	31.87

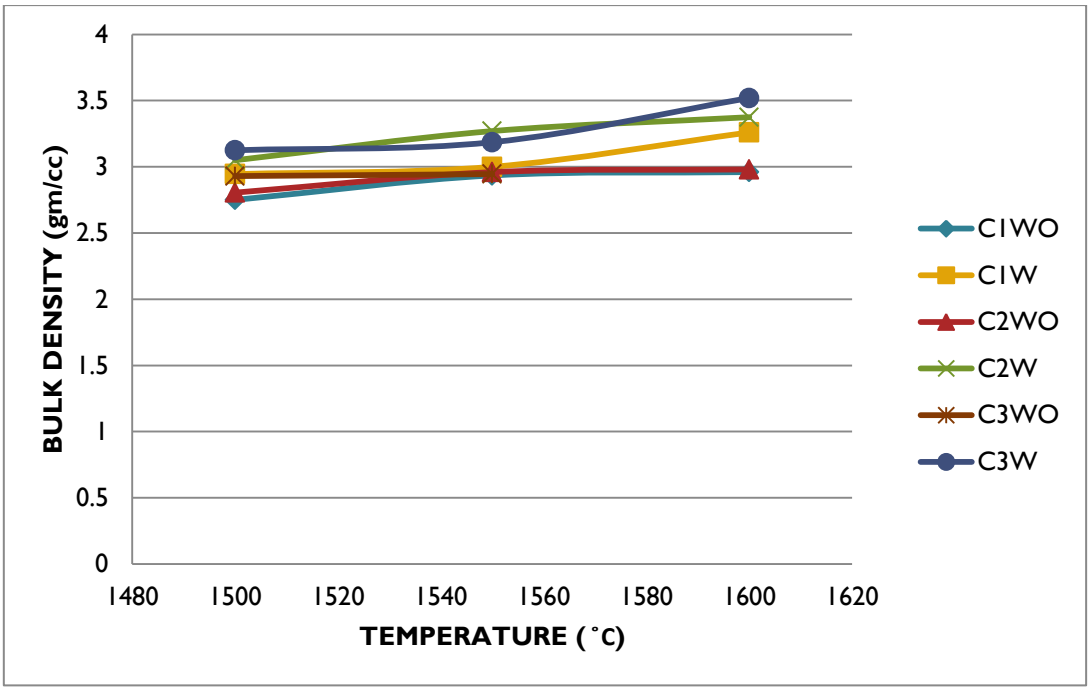
Shrinkage is in %



Calculation of BD

COMP/TEMP(˚C)	C1WO	C1W	C2WO	C2W	C3WO	C3W
1500	2.75	2.94	2.80	3.05	2.93	3.125
1550	2.935	3.0	2.945	3.186	2.96	3.27
1600	2.96	3.26	2.98	3.375	2.99	3.52

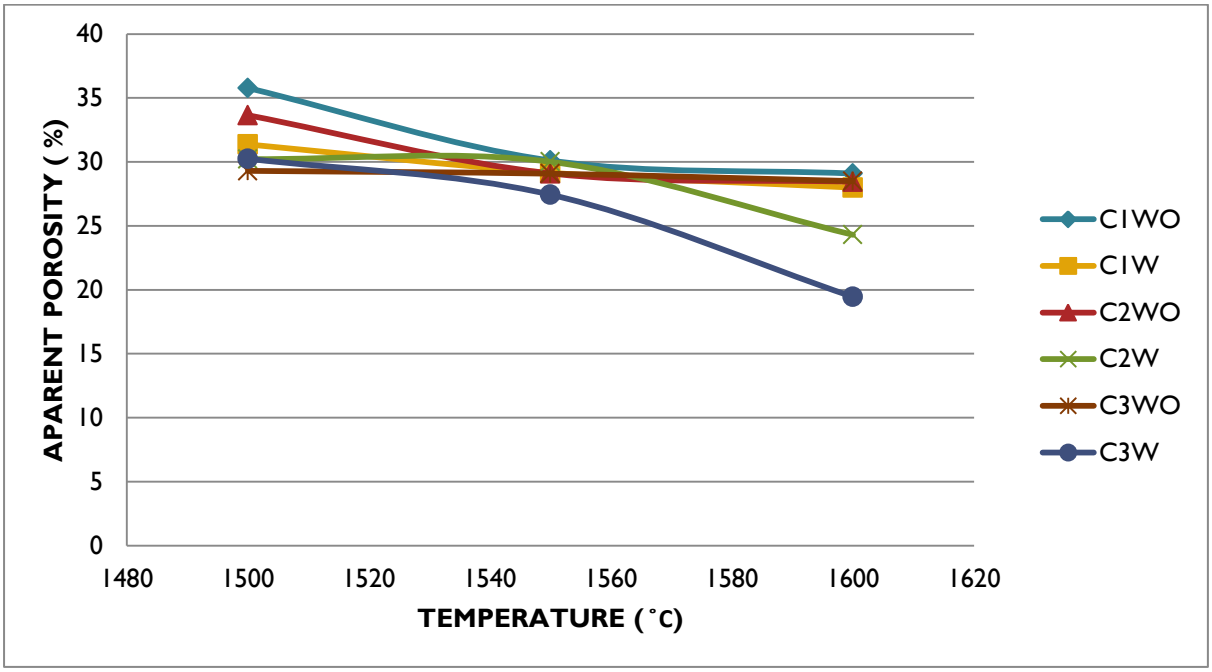
BD is in gm/cc



Calculation of AP

COMP/TEMP(˚C)	C1WO	C1W	C2WO	C2W	C3WO	C3W
1500	35.78	31.37	33.65	30.22	29.3	30.25
1550	30.11	29.15	29.1	30.01	29.08	27.44
1600	29.09	27.99	28.45	24.3	28.5	19.45

AP is in %



CONCLUSION

- Spinelization was studied at three different temperatures (600˚C, 700˚C & 800˚C) and definite spinel peak was observed at 700 ˚C via auto-combustion synthesis process using metal : glycine ratio as 1: 2, 1:2.22, 1:2.5 .
- Metal: glycine ratio i.e.1:2.5 has higher peak due to high fuel ratio.
- Cr_2O_3 addition enhances the spinel formation and also the densification.
- Cr_2O_3 addition has high effect on composition 3 (i.e. Metal : glycine ratio 1:2.5) due to high fuel ratio.

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